# Phosphates and Phosphoric Acid

## Raw Materials, Technology, and Economics of the Wet Process

Second Edition, Revised and Expanded

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of the slurry (pumping problems). Once again, the operator has, by trial and error, to find out what is the best sulfate level for the specific installation and the rock in use.

A very important question is related to choosing the location where the sulfate analysis sample is to be taken and how to interpret the result. This depends on the characteristics of the plant: the acid and rock mixing points, the size of the compartments, and the volume of recirculated slurry. Fig. 2.38 demonstrates the problem of choosing the analysis sample location and the comparative value of the sulfate levels for two identical plants, except for differing recirculation rates, working with the same phosphate rock.

A final remark about analyses: If sampling is automatic, followed, for example, by a Technicon-type continuous analyzer, the $SO_4$ values found are close to SSL line values from hot slurry. If the samples are taken manually, filtered, and analyzed within a certain time needed for that purpose, the $SO_4$ values can vary substantially— up to about 40% lower if the sample is taken from the phosphate mixing tank.

## Effect of Impurities

The influence of impurities (in the phosphoric acid) on crystallization is undeniable. These impurities originate mainly from the phosphate rock, but some can also come from the added sulfuric acid, the process water, or even corrosion of the equipment.

Many authors think [93,94] that these impurities will be adsorbed on certain crystal faces, impeding their growth rate (mainly the fast growing faces). If so, the adsorbed impurities will have a regulating function, because with pure phosphoric acid solutions there are generally great differences in growing rates between the different faces, resulting in needle-type crystal growth.

The effect of the impurities will be only one of the many factors controlling habitus and size of the crystals. Different impurities may also create conflicting influences, and the final picture will be the result of a complicated series of interactions. For this reason it is not possible to forecast the effect of the impurities of a given phosphate rock. Trials have to be made, even though we do know some of the effects that generally occur with a given type of impurity.

The most active impurities and those which we will consider here are: $Al^{3+}$, $Fe^{3+}$, $Mg^{2+}$, $Ca^{2+}$, rare earth, organic impurities, $SO_4^{2-}$, $SiF_4^{2-}$, and $F^-$.

*Aluminum* $(Al^{3+})$. Phosphate rocks always contain some aluminum, but the content of commercial rock can vary widely, usually from 0.2 to 3% as $Al_2O_3$. Unfortunately, most of the aluminum goes into solution during the phosphate rock attack. Usually, some 70−90% of the

Free Sulfuric Acid Excess. Free sulfuric acid excess affects the solubility product and controls both $Ca^{2+}$ and $SO_4^{2-}$ concentration. Optimum crystallization speed or mass transfer is achieved when

$$na[Ca^{2+}] = n'a'[SO_4^{2-}] = maximum \qquad (22)$$

where

    n, n' = number of ions

    a, a' = activity of corresponding ion

The highest recrystallization speed often occurs with $SO_4^{2-}$ concentrations that are above those of $Ca^{2+}$; sometimes $SO_4^{2-}$ concentrations are a multiple of $Ca^{2+}$ concentrations. The $SO_4^{2-}$ : $Ca^{2+}$ ratio governing the best recrystallization speed varies with the $H_3PO_4$ concentration of the acid. Figure 2.43 shows the effect of $SO_4$ concentration on recrystallization time. The lower the $H_3PO_4$ concentration, the higher the $SO_4^{2-}$ concentration has to be to achieve optimum recrystallization speed.

Impurities. Some impurities affect recrystallization severely. Their influence can be such that recrystallization can be completely blocked and a recrystallization process becomes unserviceable because of the presence of this kind of impurity. So far, this blocking mechanism is not understood. It is supposed to be a kind of superficial ionic adsorption on active crystal surfaces, blocking further buildup. The most common impurities having such an action are fluorides, but many other elements have been noted even if they occur in very low concentrations [113].

The cycle of impurities in double crystallization systems can be very complicated and subject to uncontrolled variations. This is one of the risks that has to be taken into consideration when choosing a recrystallization process with a phosphate rock that has not yet been used in such processes. From practice it is known that sedimentary rocks recrystallize better than igneous rocks and that Tunisian and Moroccan rocks recrystallize better than Florida or Taïba rocks, probably due to the nature and the concentration of the impurities occurring in the corresponding phosphate ores [114].

Extensive work on this subject was done by Uusitalo et al. in Finland, where they tried to operate a hemihydrate plant with igneous rocks [115]. It was found that lanthanum ($La^{3+}$), cerium ($Ce^{4+}$), and possibly aluminum affected the speed of recrystallization. In the hemihydrate phase lanthanum and cerium move into the solid phase,

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | ) PATENT |
| | ) |
| Mohamed TAKHIM | ) GROUP: 1793 |
| | ) |
| Serial No.: 10/583,344 | ) EXAMINER: QIAN, Yun |
| | ) |
| Filed: August 4, 2006 | ) CONFIRMATION NO. 3133 |
| | ) |
| METHOD FOR ETCHING PHOSPHATE | ) CUSTOMER NO. 25269 |
| ORES | |

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## DECLARATION UNDER 37 C.F.R. §1.132

I, Marc Sonveaux, who resides at rue de la Vôte 36, B-5030 Gembloux, Belgium, hereby declare as follows:

1. I am a chemical engineer graduate of the Université Catholique de Louvain in Louvain la Neuve, Belgium, with 9 years of experience in research and development and industrialization in the chemical industry. I am the Research and Development Manager for EcoPhos sa in Louvain la Neuve, Belgium. EcoPhos sa is an organization which researches processes applicable to the phosphate industry.

2. I am familiar with the above-identified U.S. patent application and I have read the non-final Office Action of November 17, 2009, wherein the examiner has rejected claim 15 (the independent claim) and claims 2-5, 7, 9-11 and 14 (dependent claims) as being obvious over Hauge et al. (U.S. Patent No. 3,919,395). I am aware of the examiner's

opinion that the change in sequence of neutralization in the present method compared to that in Hauge et al.

3. I have conducted the following experimentation to demonstrate that the difference in neutralization steps is significant and unexpected, and certainly not obvious.

Comparison of Methods

In the previous declaration we have compared the present method with the method of Hauge et al.

The main difference between both methods consists in the process sequence

| Present Method | Hauge et al. |
|---|---|
| 1. Digestion with dilute HCl | 1. Digestion with dilute HCl |
| 2. Preliminary neutralization | 2. Filtration 1 |
| 3. Filtration 1 | 3. Preliminary neutralization |
| 4. Subsequent neutralization with DCP precipitation | 4. Filtration 2 |
| 5. Filtration 2 | 5. Subsequent neutralization with DCP precipitation |
| | 6. Filtration 3 |

We have shown that this difference is essential because the properties of the process and the quality of the final product are greatly modified.

It resulted from this comparison that a rock digestion with pre-neutralization, without intermediary filtration, is in an unexpected manner substantially more advantageous than a method with intermediary

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filtration after digestion and before pre-neutralizing (in term of purity, yield and process complexity).

The process conditions used for the present method on this experimentation will be called the conditions of the base case.

The present declaration consists on comparing the behaviour of the different processes at the limits and outside of the limits of the process specification as described in the claims of the patent application 10/583,344:

Table I

| Parameter | Min | Base case | Max | Unit |
|---|---|---|---|---|
| Pre-neutralisation pH (first pH) | 0.8 | 1.1 | 4.0 | - |
| $P_2O_5$ content of rock | >20 | 29 | 35 | % |
| Concentration of HCl | 3.0 | 6.0 | <10.0 | % |
| Temperature of reaction | 20 | 60 | 80 | °C |

**We have shown that the present process allows having a higher purity compared to the Hauge process. This surprising difference of behaviour is thought to be due to an adsorption of the impurities on the particles of "rock digestion residue" during the pre-neutralization step in the present process (without intermediate filtration). In the Hauge process, the particles of "rock digestion residue" are removed before the pre-neutralisation step in the filtration 1. Therefore, the impurities cannot be adsorbed thereon during the pre-neutralisation.**

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The phenomenon of adsorption of impurities on digestion residue is known in other applications like the classical wet process where the rock is digested in sulphuric acid. In this case, it is well known that the residue can adsorb impurities (*Pierre Becker, Phosphates and phosphoric acid, Fertilizer science and technology – Vol. 6, Marcel Dekker, INC, 1989; pg 126 and 141*).

In the Hauge et al. process, the yield (ratio $P_2O_5$ in the measured product / P2O5 of the rock) was also shown to be affected by an intermediate filtration. This difference is due to a higher precipitation of phosphate salt during the pre-neutralisation, most likely because no residue of rock is present, resulting in a higher loss during the second filtration.

In the case of Hauge, no residue of rock is present in the pre-neutralisation step which is carried out on a filtrate obtained from filtration 1. The base (i.e. Ca compound) added will react with F to form $CaF_2$ but also with $PO_4$, while forming some solid DCP ($CaHPO_4.2H_2O$). This solid DCP is removed by the filtration 2 and thus giving loss of $P_2O_5$ in the filtration cake.

In the case of the present process, the pre-neutralisation is performed in presence of rock residue. The Ca compound of the base will react not only with F and $PO_4$ but also with other compounds present in the etching liquor for example $SO_4$ (formation of solid gypsum). This results in the formation of a solid residue that contains less absolute amount of $P_2O_5$

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than with the Hauge process and thus gives less $P_2O_5$ loss and thus a higher yield.

The relation between the purity and yield versus the amount of residue is as follows:

**High amount of residue from rock → higher purity of the liquid phase** in the present invention compared to Hauge et al.

**AND**

**High amount of residue from rock → higher yield of pre-neutralisation** in the present invention compared to Hauge et al.

The experiments were done using the following protocol:

<u>Present Method</u>

A. <u>Digestion of the rock</u>

1. Mix water with HCl 33%, to get the selected HCl concentration

2. Heat the HCl solution to 60°C and maintain at this temperature during the reaction.

3. Add the calculated amount of phosphate rock.

4. Agitate for 30 min.

5. Adjust the pH to the targeted pH with a milk of lime slurry (preliminary neutralization).

6. Agitate for 30 min.

7. Filter the liquor (Filtration 1).

8. Analyze the obtained monocalciumphosphate (MCP) solution.

## B. Production of DCP

1. Take 500 g of the filtrate of the previous step.

2. Adjust the pH to 3.2 with a milk of lime slurry (subsequent neutralization) and precipitate dicalciumphosphate (DCP).

3. Separate the DCP from the $CaCl_2$ solution by filtration (filtration 2).

4. Wash the obtained DCP with 1 X its mass of water.

5. Analyze the obtained DCP.

## Hauge et al. Method

### A. Digestion of the rock

1. Mix water with HCl 33%, to get the selected HCl concentration

2. Heat the HCl solution to 60°C and maintain at this temperature during the reaction.

3. Add the calculated amount of phosphate rock.

4. Agitate for 30 min.

5. Filter the liquor (Filtration 1).

6. Adjust the pH to the targeted pH with a milk of lime slurry (preliminary neutralization).

7. Agitate for 30 min.

8. Filter the slurry (Filtration 2)

9. Analyze the obtained monocalciumphosphate (MCP) solution.

### B. Production of DCP

1. Take 500 g of the filtrate of the previous step.

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2. Adjust the pH to 3.2 with a milk of lime slurry (subsequent neutralization) and precipitation of dicalciumphosphate (DCP).

3. Separate the DCP from the $CaCl_2$ solution by filtration (Filtration 3).

4. Wash the obtained DCP with 1 X its mass of water.

5. Analyze the obtained DCP.

For comparison, we consider the sum of F and Fe (major impurities) in final product as an indicator of purity. The yield was calculated as the quantity of $P_2O_5$ in the final product divided by the quantity of $P_2O_5$ entering the process, expressed in %.

The following paragraphs demonstrate the impact of the process parameters on those phenomena.

**Pre-neutralisation pH (first pH)**

Based on experiment and description of the patent application 10/583,344, the curve of the impurities as a function of the pre-neutralisation pH is presented in table 2.

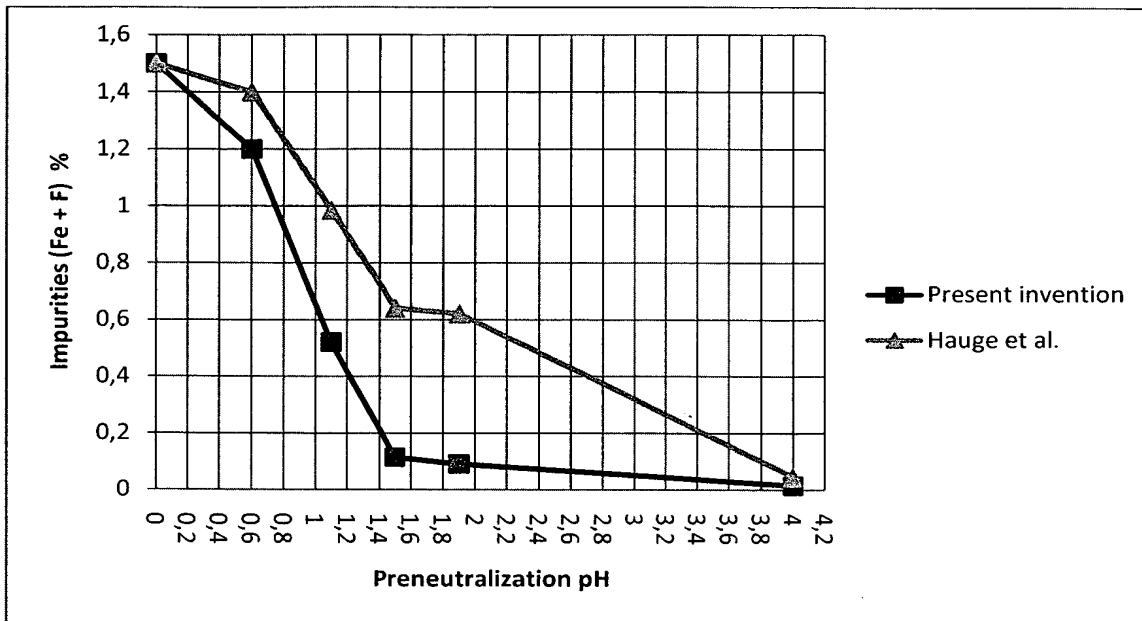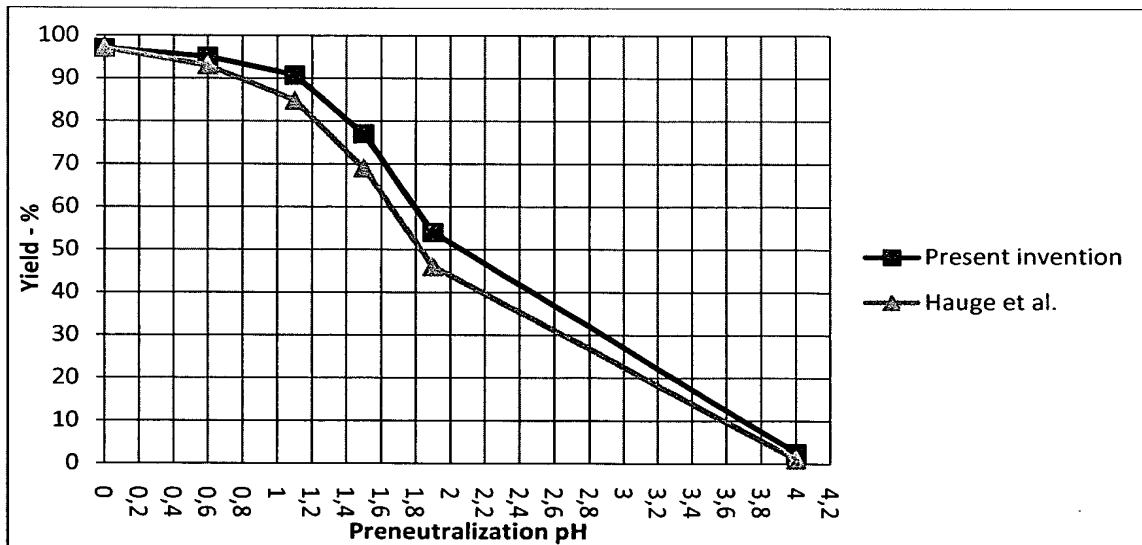The impact of the Yield is presented in table 3.

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Table 2



Table 3



The purity is measured in the present process, after pre-neutralisation, in the filtrate of filtration 1. In the Hauge et al process, the purity is measured, after pre-neutralisation, in the filtrate of filtration 2.

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In the present process, the residue of rock and the residue of pre-neutralisation will be separated in the same and only filtration step (filtration 1 of present process). Therefore, the purity obtained with the present process will always be better than the Hauge et al. process: <u>a part of impurities is adsorbed on the rock residue during pre-neutralization</u>. The highest pre-neutralisation pH gives the largest difference between both processes.

It results from table 2 that a pH lower than 0,8 does not allow sufficient purification concerning Fe and F impurities. This purification is worst with the Hauge et al process compared to the present invention.

If the pH is higher than 4, all etched phosphate will immediately precipitate and be lost in the cake of the following filtration.

In term of yield, the same effect is observed (table 3).

We have noticed that in the base case, the total yield of the digestion in the present process was of 90.7% while it was 84.8% for the Hauge et al process (see my previous declaration).

If no pre-neutralisation is performed, the yield is maximised. Effectively there is no DCP precipitation, but the content of impurities is too high.

If the pre-neutralisation pH increases, the global yield of both process decreases in parallel. Due to the presence of residue of rock in the present process, less $P_2O_5$ is co-precipitated during the pre-neutralisation

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step resulting in a yield of the present process constantly higher than Hauge et al.

If the pH is higher than 4, all the etched phosphate precipitates and is lost in the cake of the following filtration. The yield becomes too low.

### $P_2O_5$ content of rock

If the $P_2O_5$ content of rock is very low, the amount of non-dissolved rock is high. More impurities can therefore be adsorbed on the residue surface in the present process and less $P_2O_5$ is precipitated. The impurity level in the DCP produced while using the present process will be lower and the yield higher (table 4).

Table 4

| 29% $P_2O_5$ in rock | | |
|---|---|---|
| | **Present invention** | **Hauge et al.** |
| **Yield (% w/w)** | 90.7 | 84.8 |
| **Impurities (F+Fe in% w/w)** | 0.52 | 0.98 |

If the $P_2O_5$ of the rock is high, the purity of the DCP is higher. In the present process, the adsorption of impurities at the surface of rock remains present. Less impurities will be present in the final product using the present technology.

The yield of the present process remains higher as residue is still present (table 5).

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Table 5

| 33% P$_2$O$_5$ in rock | Present invention | Hauge et al. |
|---|---|---|
| Yield (% w/w) | 92.0 | 90.0 |
| Impurities (F+Fe in% w/w) | 0.03 | 0.05 |

**Concentration of HCl**

If the concentration of HCl is higher than 10%, the disadvantages disclosed on page 1, line 29 to page 2, line 4 of the specification begins to take place.

If the concentration of HCl is high (but less than 10%), a lot of rock will be digested. The yield will be high and the impurities will be dissolved. Anyway, some residue remains un-dissolved and can adsorb the impurities during pre-neutralisation in the present process. Therefore the DCP produced is more pure with the present process. The difference of yield remains between both processes: the yield of the present process will be higher.

Table 6

| 10% HCl | Present invention | Hauge et al. |
|---|---|---|
| Yield (%) | 90.3 | 88.7 |
| Impurities (F+Fe in% w/w) | 0.50 | 0.78 |

If the concentration of HCl is low, the amount of non-dissolved rock is high. This results on a higher adsorption of the impurities for the present

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process and then on a better purity compared to Hauge et al. In the present process the yield remains higher.

Table 7

| 6% HCl | | |
|---|---|---|
| | **Present invention** | **Hauge et al.** |
| **Yield (%)** | 90.7 | 84.8 |
| **Impurities (F+Fe in% w/w)** | 0.52 | 0.98 |

**Temperature**

The temperature has a low influence on digestion behaviour. The amount of residue of digestion remains the same between 20 and 80°C. Therefore this parameter doesn't influence the Present invention nor the Hauge et al. invention.

**pH DCP prescipitation (second pH)**

The step of DCP precipitation is performed after the removal of the rock residue and the pre-neutralisation residue. (filtration 1 in the present process and filtration 2 in the Hauge et al. process).

In any case, the filtrate of the rock digestion step will be more pure using the present process.  This difference of purity will remain at the DCP precipitation step.

It is a well known fact that the presence of impurities may affect the crystallisation of a product.  This is demonstrated for the case of gypsum in *Pierre Becker, Phosphates and phosphoric acid, Fertilizer science and*

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*technology – Vol. 6, Marcel Dekker, INC, 1989; pg 126*: "The influence of impurities on crystallisation is undeniable".

A good crystallisation of DCP will allow a more complete precipitation of the $P_2O_5$, a better filtration and so a better yield. In the case described in the previous declaration, a difference of yield was observed for the DCP precipitation between the EcoPhos process and Hauge et al. process. This difference is probably linked to a better efficiency of crystallisation using a more pure MCP solution as obtained without intermediate filtration steps in the present process.
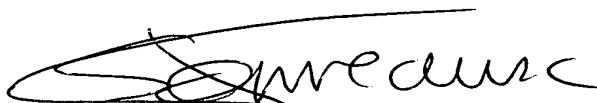
Table 8

| | Present invention | Hauge et al. |
|---|---|---|
| **Impurities in MCP (F+Fe in% w/w)** | 0.044 | 0.092 |
| **Yield of DCP precipitation (%)** | 99.9 | 89.7 |
| **Impurities in DCP (F+Fe in% w/w)** | 0.52 | 0.98 |

It results from this comparison that a rock digestion with pre-neutralization, without intermediate filtration, is confirmed to be substantially more advantageous than a method with intermediate filtration after digestion and before pre-neutralizing: The purity is higher due to an adsorption of the impurities at the surface of the rock residue particles in the present process that doesn't occur in Hauge et al. process. The yield is also higher in the present process due to a lower precipitation of $P_2O_5$ due to the interaction of the rock residue and the calcium base compound used for pre-neutralisation.

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The crystallisation of DCP in the neutralisation step is better with the present process as the MCP solution is more pure.

I furthermore declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon.

Marc Sonveaux

02/03/2010

Date

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